Solid-State Inorganic Nanofiber Network-Polymer Composite Electrolytes for Lithium Batteries

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Project ID: ES321

Overview

Timeline

- Project Start Date: Oct. 1, 2016
- Project End Date: Sept. 30, 2019
- Percent complete: 20%

Barriers

- Poor conductivity of current composite electrolytes
- Low mechanical strength of composite electrolytes
- Low stability during operation

Budget

- Total project funding
  - DOE share:$1,244,012
  - Contractor share: $156,181
- Funding received in FY 2016: $479,720
- Funding for FY 2017: $463,711

Partners

- Interactions/collaborations:
  North Carolina State University
- Project lead:
  West Virginia University (WVU)

Relevance

Overall objectives

Develop the solid-state electrolytes by integrating a highly-conductive inorganic nanofibrous network in a conductive polymer matrix for both lithium metal and lithium-sulfur batteries.

Objectives of this period

- **Fabricate the inorganic nanofibers with electrospinning technique; and improve the ionic conductivity of inorganic nanofibers.**
- **Develop ionic-conductive polymers.**

Impact

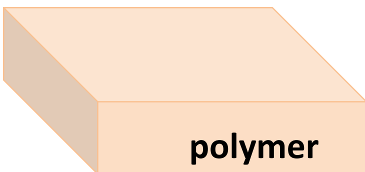
The proposed DOE funding will allow the research team to conduct the research and development of solid-state inorganic nanofiber-polymer composite electrolytes that will not only provide higher ionic conductivity, improved mechanical strength and better stability than the PEO-based polymer electrolyte, but also exhibit better mechanical integrity, easier incorporation and better compatibility with the lithium metal anode than the planar ceramic membrane counterparts. The proposed inorganic nanofiber-polymer composite electrolytes will enable the practical use of high energy-density, high power-density lithium metal batteries and lithium-sulfur batteries.

Milestones

Task	Description	Year 1				Year 2			
		Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Task 1.1	Develop inorganic nanofibers								
M1.1.4	Ionic conductivity >1.0 mS/cm								
Task 1.2	Develop polymers								
M1.2.4	Ionic conductivity >0.2 mS/cm								
Task 2.1	Synthesize composite electrolytes								
Task 2.2	Characterize composite electrolytes								
Task 2.3	Measure properties of composite electrolyte								
M2.3	Conductivity >0.8 mS/cm, decomposition voltage >4.5 V vs. Li^+/Li								
Tasks 2.4 - 2.7	Optimize composite electrolytes								

Approach

Develop inorganic nanofiber-polymer composite electrolytes



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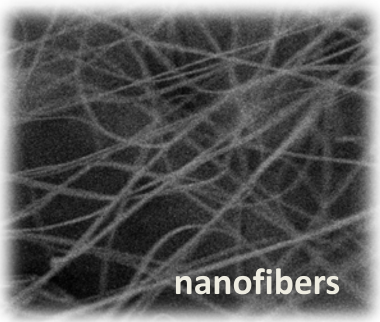
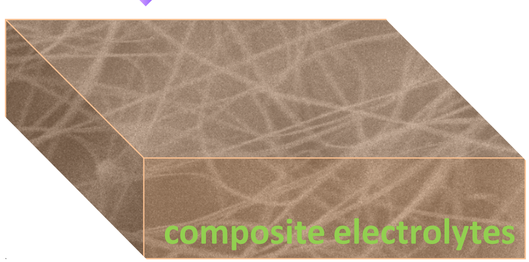




Develop the block copolymers or cross-linked polymers that have higher ionic conductivity than traditional polyethylene oxide (PEO) polymers.

Go/ No-Go: Approach identified to optimize ion-conducting polymers and inorganic nanofibers.

PY16 Q4 | PY17 Q1 | FY17 Q2 | FY17 Q3 (Year 1)

Go/ No-Go: Approach identified to optimize development composite electrolytes.

Develop and improve the ionic conductivity of inorganic nanofibers

- **Provide continuous Li^+ transport channels via nanofiber network**
- **Inhibit crystallization of amorphous polymer electrolyte.**
- **Facilitate lithium salt dissociation and ion transport through the polymer electrolyte**

FY17 Q4 | FY18 Q1 | FY18 Q2 | FY18 Q3 (Year 2)

Develop nanofiber-polymer composites

- **In-situ polymerization**
- **Design linker to couple the nanofibers to the polymer matrix**
- **Design deliberately to suppress the formation of lithium dendrites**
- **Measure the mechanical and electrochemical properties of composites**
- **Optimize the nanofiber-polymer composites**

Technical Accomplishments & Progress

This project started six months ago. We have accomplished the following tasks during last six months (Oct. 1, 2016 ~ April 10, 2017):

(i) Synthesized three precursors and monomers for block co-polymers.

(ii) Prepared a block-copolymer and tested its ionic conductivity.

(iii) Synthesized and characterized the $Li_{0.33}La_{0.56}TiO_3$ (LLTO) nanofibers with electrospinning technique, retained the fiber shaper after calcination of the electrospun nanofibers, and achieved the desired single-phase perovskite structure after calcination.

(iv) Fabricated and characterized the Garnet-type $Li_{7-3y}Al_yLa_3Zr_2O_{12}$ (LLAZO) nanofibers with electrospinning technique, achieved the desired single-phase cubic structure after calcination of the electrospun nanofibers. We are adjusting the sintering condition to retain the fiber-shape after calcination.

(v) Prepared and characterized the NASICON-type $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ (LATP) nanofibers with electrospinning technique, achieved the >90% desired phase structure after calcination of the electrospun nanofibers. We are adjusting the sintering condition to retain the fiber-shape and to achieve the desired crystal phase after calcination.

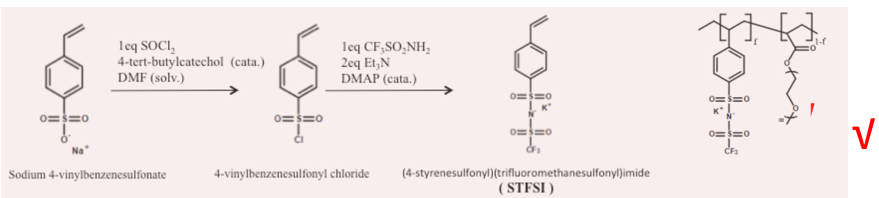
(vi) Made an initial testing of the ionic conductivity of the inorganic nanofiber-polymer composites.

Technical Accomplishments & Progress

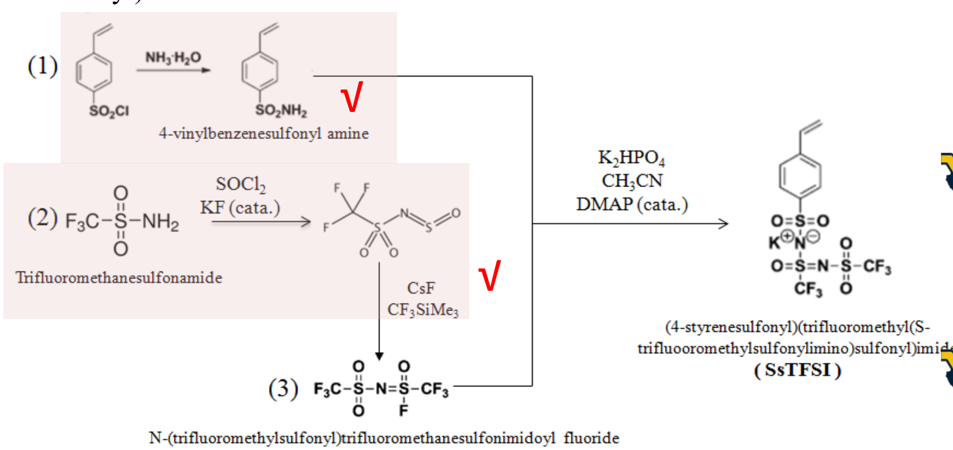
Polymer matrix:

- Synthesized monomer and copolymer
- Tested the ionic conductivity of copolymer

STFSI (4-styrenesulfonyl)(trifluoromethanesulfonyl)imide



SsTFSI (4-styrenesulfonyl)(trifluoromethyl(S-trifluooromethylsulfonylimino)sulfonyl)imide

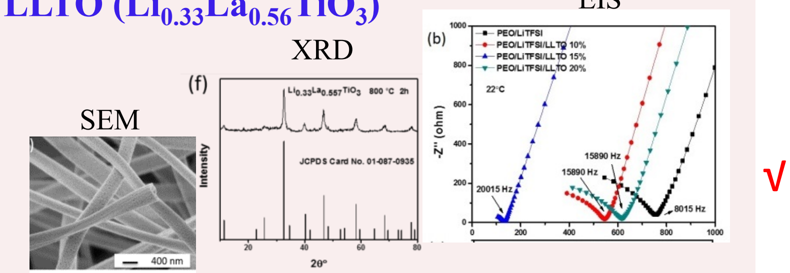


√ and pink markers indicate completed works.

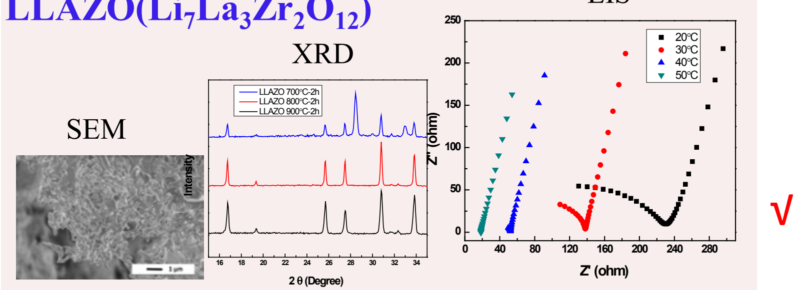
Inorganic Li-ion conductors:

- Fabricated three-types of inorganic nanofibers
- Characterized and tested ionic conductivity of PEO based composite electrolytes

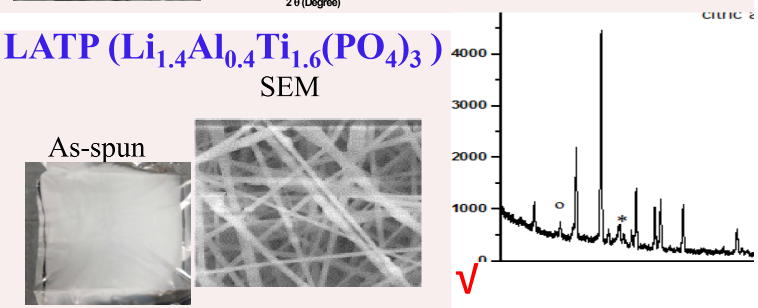
LLTO ($Li_{0.33}La_{0.56}TiO_3$)



LLAZO($Li_7La_3Zr_2O_{12}$)



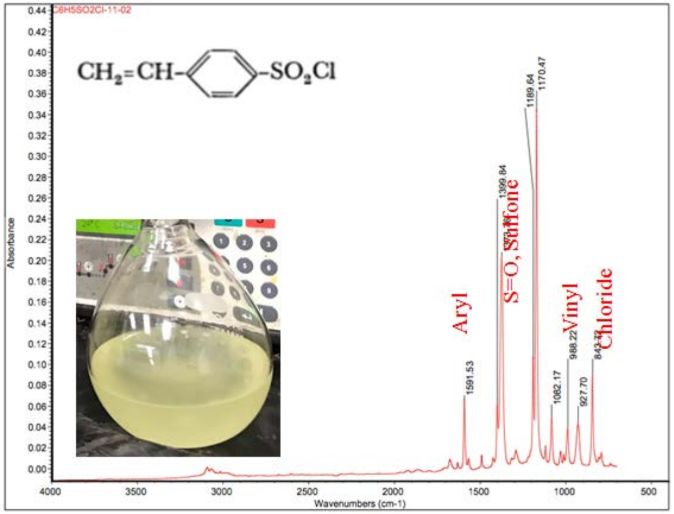
LATP ($Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$)



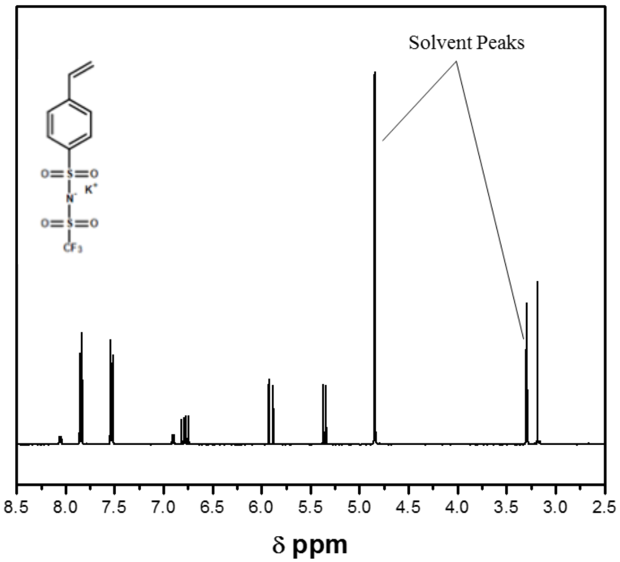
Polymer matrix development – Monomer synthesis

STFSI ((4-styrenesulfonyl) (trifluoromethanesulfonyl)imide)

Fourier transform infrared spectroscopy (FTIR) and 1H NMR was used to verify the reaction products.



- All characteristic peaks for 4-vinylbenzenesulfonyl chloride were determined in FTIR spectrum
- 1580 (aryl), 1360 (S=O), 980, 910 (vinyl), and 843 (Chloride) [cm^{-1}].



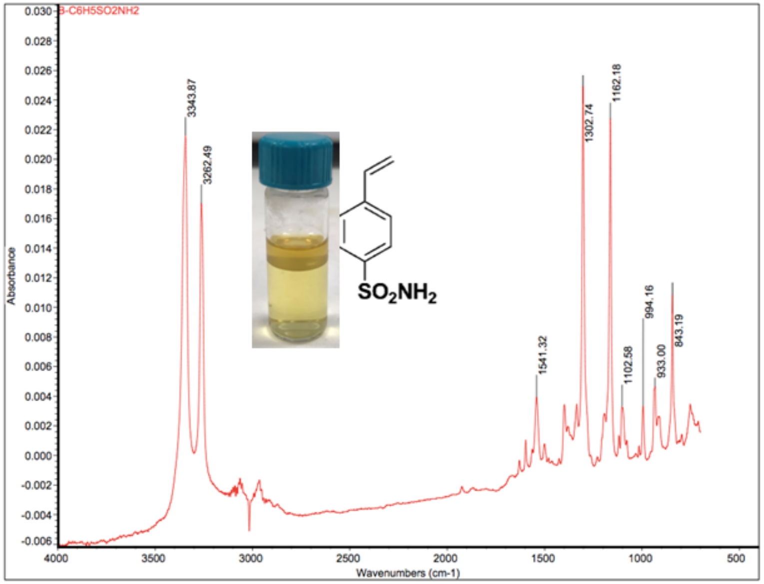
^{1}H NMR (400 MHz, DMSO-d_6, δ ppm: 7.83 (d, 2H); 7.54 (d, 2H); 6.79 (q, 1H); 5.93 (d, 1H); 5.38 (d, 1H).

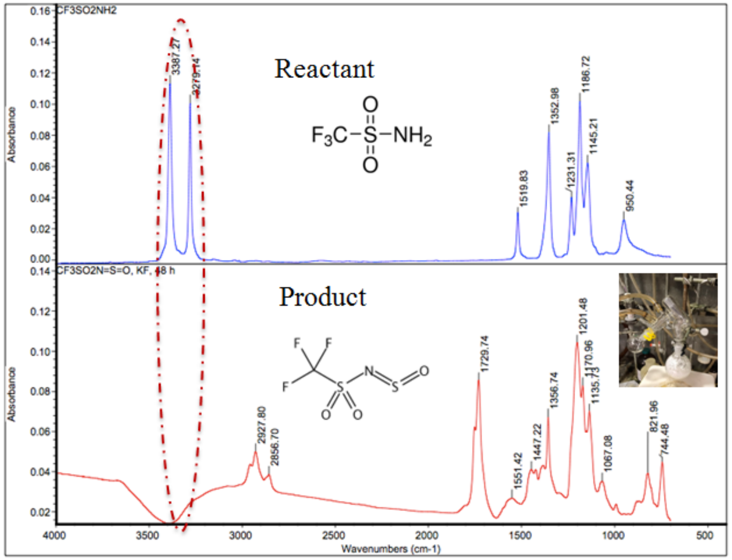
Technical Accomplishments & Progress

Polymer matrix development – Monomer synthesis

SsTFSI: (4-styrenesulfonyl)(trifluoromethyl(S-trifluooromethylsulfonylimino)sulfonyl)imide

FTIR was used to verify the reaction products.





- All characteristic peaks for 4-vinylbenzenesulfonyl chloride were remained the same
- 1591 (aryl), 1399 (S=O), 988, 927 (vinyl), 843 (Chloride) [cm^{-1}]
  - With additional peaks

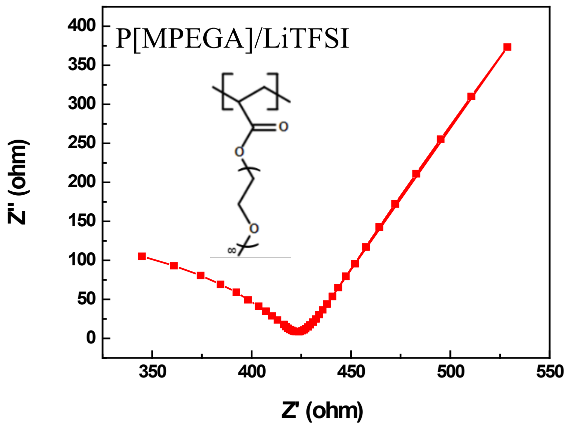
  3343, 3262 (N-H) as amide

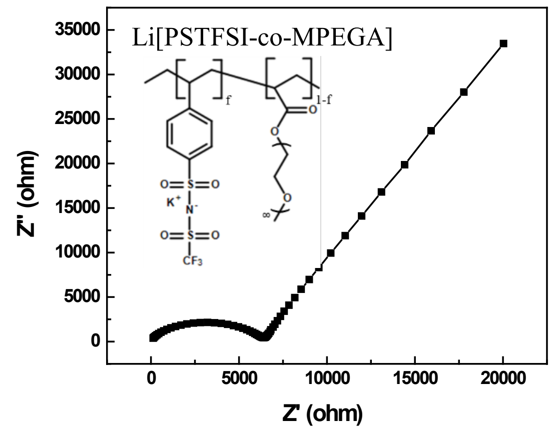
- Reaction was successful by adding catalyst KF
- Remain the same functional groups:
  - 1231,1145, 950 (C-F)
  - 1352, 1186 (S=O)
- With no amide (NH_2) peak ~3200 peaks in spectrum of assumed product

Technical Accomplishments & Progress

Polymer matrix development:

- **Synthesized potassium poly[(4-styrenesulfonyl) (trifluoromethanesulfonyl)imide-co-methoxy-polyethylene glycol acrylate] (K[PSTFSI-co-MPEGA]) copolymers with different [EO]/[K+] ratios,**
- **Tested the (Li[PSTFSI-co-MPEGA]) (EO/Li^+ = 30), achieving conductivity of 1.16 × 10^{-6} S/cm.**





Electrochemical impedance spectra (EIS) of (a) homopolymer electrolyte (P[MPEGA]/LiTFSI) (EO/Li^+ = 20) and (b) copolymer electrolyte (Li[PSTFSI-co-MPEGA]) (EO/Li^+ = 30).

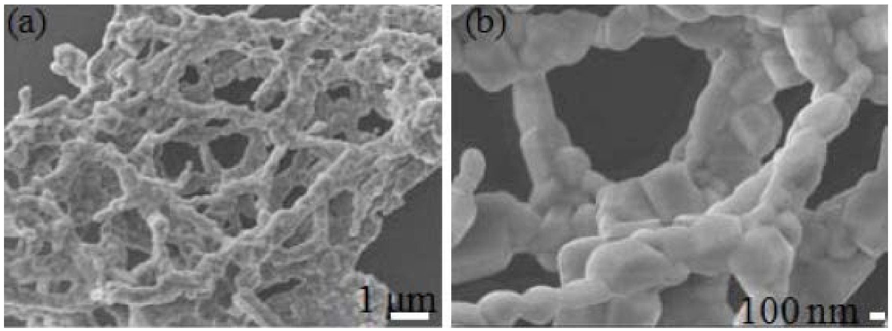
Samples	Feed EO/K^+ Ratio	Actual EO/K^+ Ratio	Ionic Conductivity S/cm
Copolymer K[PSTFSI-co-MPEGA]			
Polymer 1	32.00	30.30	1.16 × 10^{-6}
Polymer 2	24.00	23.10	To be tested
Polymer 3	16.00	20.26	To be tested

EO/K^+ ratio: MPEGA/PSTFSI ratio

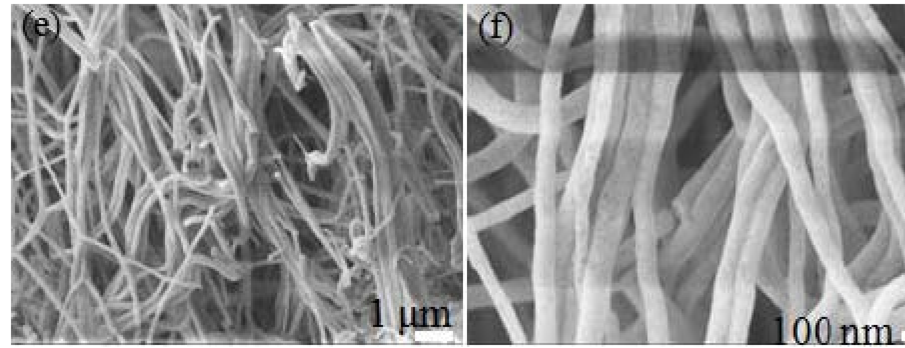
Accomplishments and Progress

Inorganic nanofiber development:

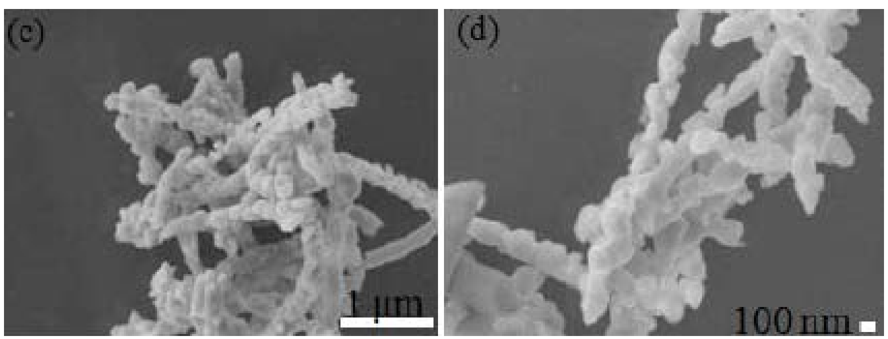
- **Perovskite-type oxide, $Li_{0.33}La_{0.56}TiO_3$ (LLTO)**



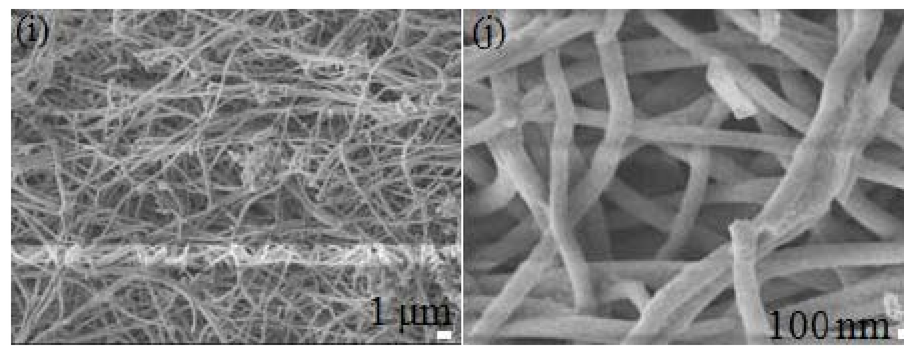
After calcination at 1000 °C



After calcination at 800 °C



After calcination at 900 °C



After calcination at 700 °C

SEM images of the electrospun nanofibers after calcination at different temperatures

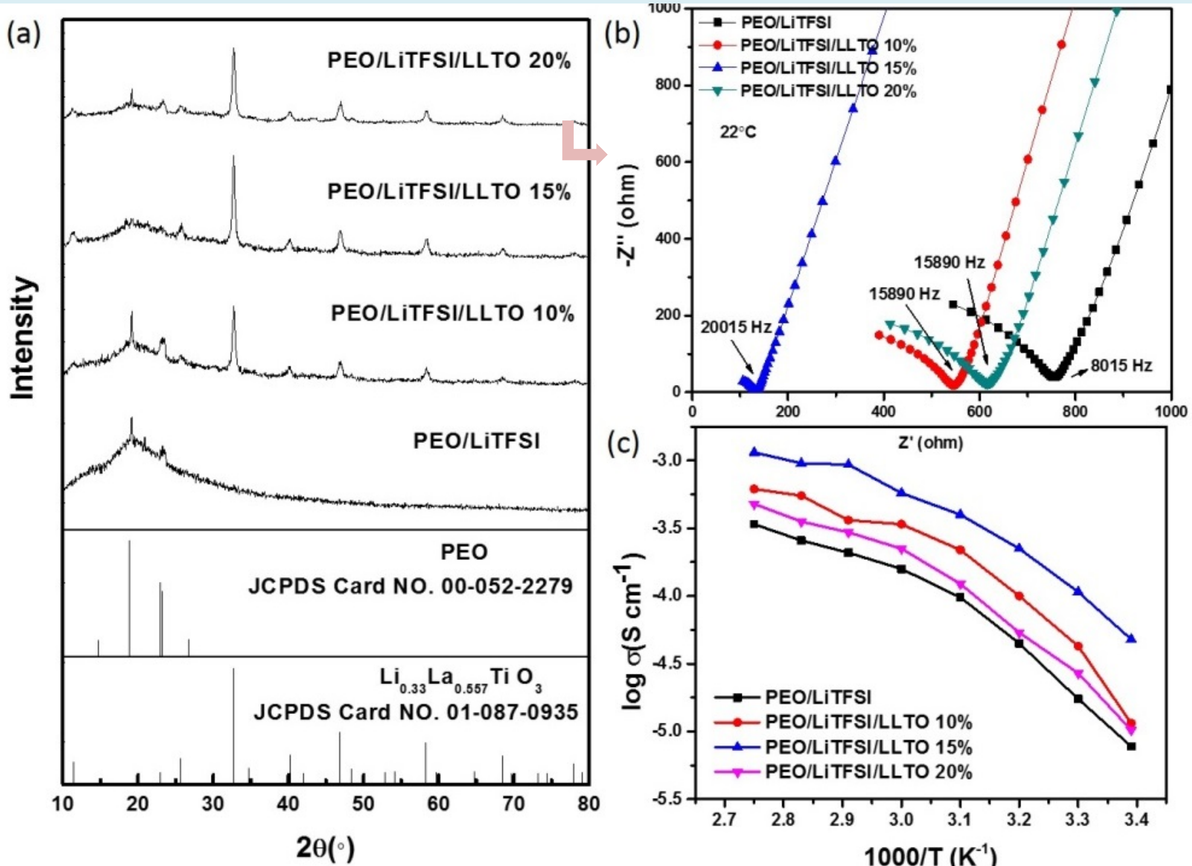
After calcination of the electrospun nanofibers at 800 °C, the material retained the fiber-shape and achieve single-phase perovskite. In short, we have successfully fabricated the LLTO nanofibers.

Accomplishments and Progress

Inorganic nanofiber development:

- **Perovskite-type oxide, $Li_{0.33}La_{0.56}TiO_3$ (LLTO)**

PEO/LiTFSI/15wt% LLTO composite electrolyte demonstrated a resistance of 133.3 Ω, achieving the ionic conductivity of 4.76×10^{-5} S/cm at room temperature.



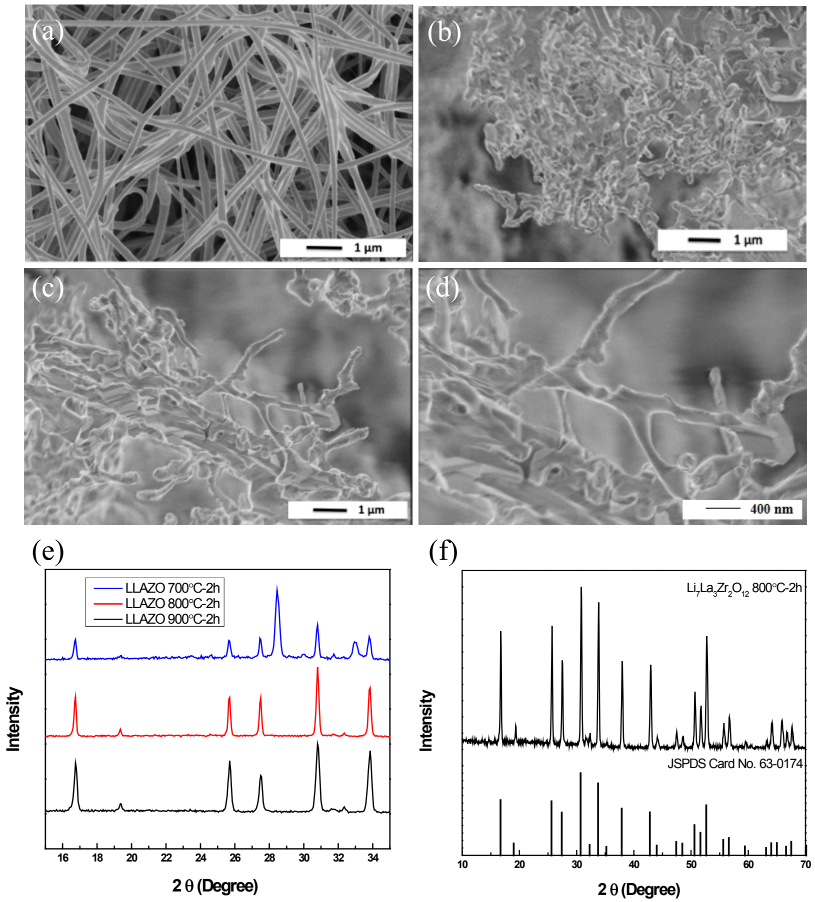
XRD profiles of PEO/LiTFSI/LLTO composites.

Conductivity measurement for PEO/LiTFSI/LLTO composites

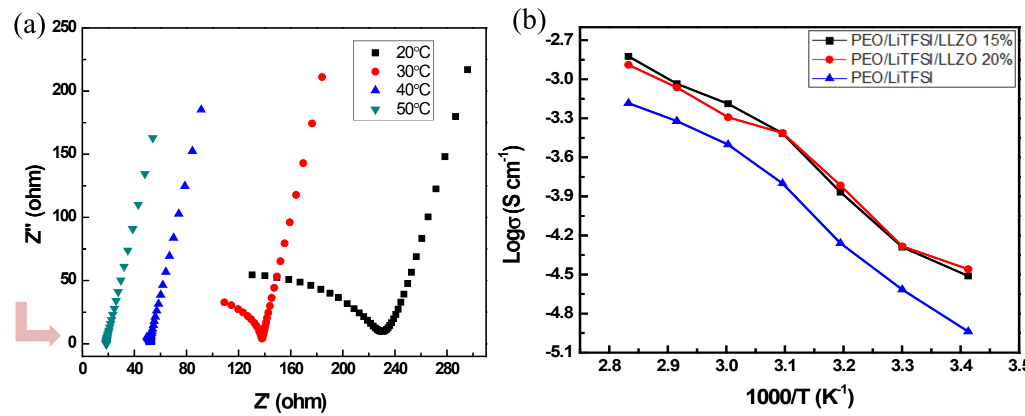
Accomplishments and Progress

Inorganic nanofiber development:

- **Garnet-type oxide, aluminum-doped $Li_7La_3Zr_2O_{12}$(LLAZO).**



The PEO/LiTFSI/15wt% LLAZO nanofiber composite electrolyte exhibited ionic conductivity of 3.47×10^{-5} S/cm.



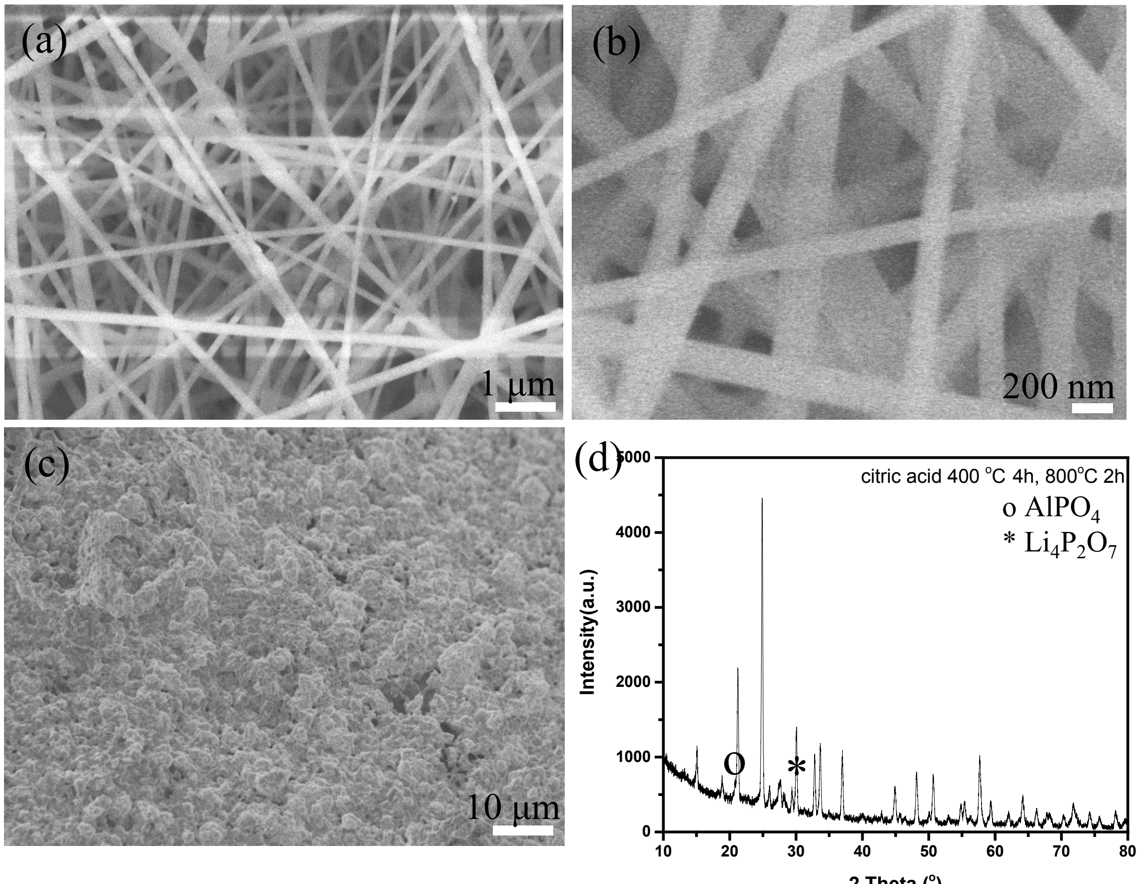
(a) EIS profiles of PEO/LiTFSI/15wt% LLAZO electrolyte at different temperatures of 20, 30, 40 and 50 ^{o}C,

(b) temperature dependence of ionic conductivity of PEO/LiTFSI/LLAZO electrolyte with different LALZO filler contents in the temperature range of 20-90 ^{o}C.

Pure cubic LLAZO phase obtained at 800 ^{o}C and 900 ^{o}C. SEM images of (a) as-spun nanofibers and (b-d) the corresponding LLAZO nanofibers calcinated at 800 ^{o}C. (e) XRD patterns of LLAZO nanofibers (nitrate precursor) calcinated at different temperatures and (f) XRD profile of cubic $Li_7La_3Zr_2O_{12}$ (LLZO) phase (JCPDS card 63-0174).

Inorganic nanofiber development:

- **NASICON-type phosphate, $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP)**



LATP nanofibers have been synthesized by electrospinning. However, the phase and morphology of the calcinated product need to optimized

SEM images of (a) (b) as-spun nitrate precursor nanofibers and (c) the corresponding LATP nanofibers calcinated at 800 °C, (d) XRD pattern of LATP inorganic nanofibers.

Responses to Previous Year Reviewers' Comments

- This project just started six months ago. There is no any previous comment.

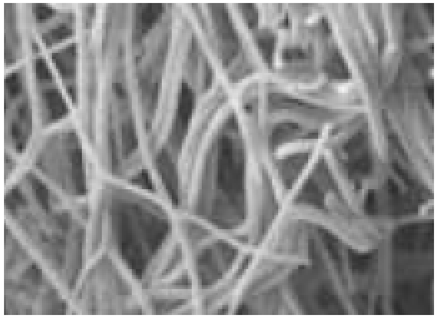
Partners/Collaborations

U.S. DEPARTMENT OF ENERGY	**U.S. Department of Energy** -Sponsorship, steering
West Virginia University	**West Virginia University - Project lead** Management and coordination; inorganic nanofiber design, synthesis and characterization; composite electrolyte development; and half cell construction and testing
NC STATE UNIVERSITY	**North Carolina State University - Key partner** Polymer matrix design, synthesis and characterization; linker development; and full cell construction and testing

Remaining Challenges and Barriers

For polymer matrix:

- The ionic conductivity of STFSI-based copolymers needs to be further improved by design



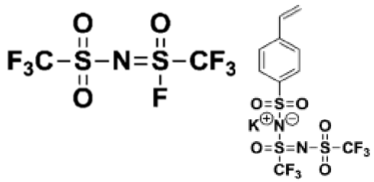
For inorganic nanofibers:

- The calcination process needs to be optimized to retain the fiber-shape of the calcinated LLAZO nanofibers.
- The crystal phase and morphology of the LATP nanofibers needs to be tuned to achieve high ionic conductivity.

Proposed Future Work

Polymer matrix:

- Reduce the EO/Li+ ratio, and forma block copolymer
- Synthesize SsTFSI
- Improve the ionic conductivity of polymers



Electrospun nanofiber fillers:

- Optimize the electrospinning and calcination processes to tailor the morphology and crystal structure of nanofibers
- Test the ionic conductivity of nanofibers
- Improve the ionic conductivity of nanofibers by doping

Composite electrolytes:

- Synthesize the inorganic nanofiber-polymer composite electrolytes
- Optimize the fiber-to-polymer ratio in composite electrolytes
- Develop a linker to couple the nanofibers with the polymer matrix
- Test the ionic conductivity, the transference number and the electrochemical stability window of composite electrolytes
- Improve the ionic conductivity of composite electrolytes

Any proposed future work is subject to change based on funding levels.

Summary

Objective : Develop the solid-state electrolytes by integrating a highly-conductive inorganic nanofibrous network in a conductive polymer matrix for both lithium metal and lithium-sulfur batteries.

Approach: Integration of the highly Li^+-conductive inorganic nanofiber network into the polymer matrix not only provides the continuous Li^+ transport channels but also kinetically inhibits the crystallization from the amorphous state of polymer electrolyte. The inorganic nanofibers will be fabricated with electrospinning technique; and the ionic conductivity of inorganic nanofibers will be improved by chemical substitution or doping. Highly ionic-conductive polymers will be developed by cross-linking and/or creation of a block-copolymer structure; and the composition and microstructure of the composite electrolyte will be designed to suppress the lithium dendrite formation.

Accomplishments: (i) synthesized three precursors and monomers for block co-polymers, (ii) prepared a block co-polymer; (iii) synthesized three different types of inorganic nanofibers.

Collaboration: The work is performed at West Virginia University (WVU) and North Carolina State University (NCSU). Dr. Nianqiang (Nick) Wu at WVU serves as PI, and Dr. Xiangwu Zhang at NCSU acts as Co-PI.